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[Claim(s)]

[Claim 1] A pillar-shaped semiconductor group anisotropically arranged to a thickness direction, and fine pores continuously prolonged in a longitudinal direction of said pillar-shaped semiconductor formed of a gap between [ each ] pillar-shaped semiconductors, A chemical modification semiconductor electrode, wherein it has a \*\*\*\* air quality semiconductor electrode layer or both multi-air quality semiconductor electrode layer \*\* constituted and some or all of this pillar-shaped semiconductor group surface comes to support a functional compound.

[Claim 2] The chemical modification semiconductor electrode according to claim 1, wherein each pillar-shaped semiconductors are ten or more anisotropy factors.

[Claim 3] The chemical modification semiconductor electrode according to claim 1 or 2 which each pillar-shaped semiconductor crosses or connects mutually, forms network structure, and is characterized by things.

[Claim 4] The chemical modification semiconductor electrode according to any one of claims 1 to 3 which a pillar-shaped semiconductor group contains at least one sort of a metallic oxide chosen from titanium oxide, a zinc oxide, tin

oxide, niobium oxide, and indium oxide, and is characterized by things.

[Claim 5]The chemical modification semiconductor electrode according to any one of claims 1 to 4 which laminates both multi-air quality insulation layer on a \*\*\*\* air quality semiconductor electrode layer or both multi-air quality semiconductor electrode layer, and is characterized by things.

[Claim 6]It is a manufacturing method of a chemical modification semiconductor electrode which manufactures the chemical modification semiconductor electrode according to any one of claims 1 to 5. A manufacturing method of a chemical modification semiconductor electrode having the process of spraying raw material metallic compounds evaporated or clustered and inactive gas on a heated substrate face under a steam atmosphere, and forming a pillar-shaped semiconductor group.

[Claim 7]A process to which some or all of a pillar-shaped semiconductor surface is made to carry out chemical absorption of the silicon compound which is a manufacturing method of a chemical modification semiconductor electrode which manufactures the chemical modification semiconductor electrode according to any one of claims 1 to 5, and is expressed with a following general formula (1). A manufacturing method of a chemical modification semiconductor electrode having a process which makes it join together chemically and makes some or all of the pillar-shaped semiconductor group surface support a pigment which has a termination group of said silicon compound, and a basis which can carry out a chemical bond.

General formula (1)  $A_nR_{(s-n)}Si-L-X$  (A expresses an aryloxy group which is not replaced [ an alkoxy group which is not replaced / a halogen atom, substitution, or /, substitution, or ] among a general formula (1).) R expresses an aryl group which is not replaced [ an alkyl group which is not replaced / substitution or /, substitution, or ]. L expresses a divalent hydrocarbon group of the carbon numbers 1-20, and a divalent hetero atom content hydrocarbon group of the carbon numbers 1-20. X expresses a vinyl group which is not

replaced [ a halogen atom, hydroxyl, an amino group, a carboxyl group, an epoxy group, an isocyanate group, a sulphydryl group, substitution, or ] in expresses an integer of 1-3.

[Claim 8]A photoelectric cell which possesses at least a support electrode which laminates a conductive substrate and the chemical modification semiconductor electrode according to any one of claims 1 to 5, and is characterized by things

[Detailed Description of the Invention]

[0001]

[Field of the Invention]About the photoelectric cell which used a chemical modification semiconductor electrode, its manufacturing method, and it, in detail, this invention is performing chemical modification and relates to highly-efficientizing, the chemical modification semiconductor electrode of the high performance many air quality, its manufacturing method, and the photoelectric cell using it.

[0002]

[Description of the Prior Art]As what is called a photoelectric cell that generates electricity by using the sunlight which is an energy source of an unlimited warehouse, single-crystal-silicon; -- polycrystalline silicon; -- amorphous silicon; -- inorganic dry type system photoelectric cells using compound semiconductor [, such as cadmium telluride and indium selenide copper,]; etc., such as a p/n assembling-die photoelectric cell and a shot key type photoelectric cell, are in use, and there are some which have already been put in practical use. However, for difficulty and the problem of \*\* having large area-ization with danger, a manufacturing facility raw material being harmful and large-scale, and high amount of capital investment and administrative and maintenance expense, and spreading a photoelectric cell widely, conquest of these problems is indispensable.

Although it pointed to large-area-izing, low-pricing, safety, etc. and many photoelectric cells using an organic material had so far been proposed to this SUBJECT, there was a problem that it was remarkable and efficiency for light utilization and endurance were low compared with an inorganic dry type system photoelectric cell.

[0003]about an organic photoelectric cell, research with a dye sensitizing type photoelectrochemical cell active to the 1970s as photosynthesis imitation technology should do -- having high internal-conversion efficiency intrinsically was found out by the external sensitization mechanism by the sensitizing dye which carried out monolayer absorption to the n type oxide semiconductor surface. However, there was a problem of the little of the light absorption amount on account of a monomolecular layer and the stability of a pigment, and efficiency for light utilization and endurance were low. About the problem of the little of the light absorption amount on account of a monomolecular layer, \*\*\*\* -- \*\* -- [-- H . -- Tsubomura -- M . -- Matumura -- Y . -- Nomura -- and T . -- Amamiya -- Nature -- Vol . -- 261 -- p . -- 402 (1976) --: -- \*\*\*\* -- " -- a photoelectricity -- chemistry -- energy conversion -- " -- Tokyo Kagaku Dojin -- 1980 --]. Although the surface area of efficiency was earned by controlling the sintering degree of ZnO particles and considering it as a porous membrane and the policy referred to as reconciling monolayer absorption and the Takamitsu absorbed amount was proposed, efficiency for light utilization was at most a little less than 2%. Then, although the research and development activities of the field stagnated at this rate temporarily, Full use of a sol-gel method is made by Graetzel etc., and it is recently specific surface area (in this invention.). With the combination of the titanium oxide porous membrane which attains to 1000, and Ru complex system sensitizing dye, a definition as a ratio of effective surface area to a project area. The high efficiency for light utilization exceeding 10% which is equal to a silicon system photoelectric cell

was reported (Nature, Vol.353, p.737-1991; U.S. Pat. No. 4927721 item etc.). According to Graetzel etc., it is a thing that their wet photoelectrochemical cell (called a Graetzel type cell) is in a practical use level also not only in respect of efficiency but in respect of a life, and research and development of the dye sensitizing type photoelectrochemical cell were revived all over the world focusing on the Graetzel type photoelectric cell after this discovery.

[0004]However, the porous membrane by a sol-gel method is a sparse aggregate by imperfect sintering of particles.

There are a problem which will say that the crystallinity of particles falls if particle diameter is made small in order to earn surface area, and a problem which says that fine pores become small and electrolytic diffusion becomes difficult, and there is difficulty of the manufacturability referred to as having to control particle diameter in optimum value of about 20 nm.

sol -- although a -\*\*\*\* system has the preferred one where calcination temperature is higher to making this thoroughly burned down including a part for organicity, if too high, sintering will advance, particles will be enlarged, and there is also a problem referred to as that fine pores will be crushed. In a sol-gel method, generally it passes also in coating liquid, a reaction advances by the time, and there is also a problem of the pot life which says that thickening and solid sedimentation will take place. In order to have realized porosity by calcination of particles, contact of particles needed to be controlled and the problem low said that the mobility of the electric charge between particles is low also had a mechanical strength as a film. Although Graetzel and others is a translation which clears these problems and is realizing high efficiency and endurance by their know how, these problems are imagined to be things connected to the lowness of the reproducibility of a supplementary examination of the Graetzel cell by other researchers.

[0005]Thus, carrying out improved efficiency of the dye sensitizing type photoelectrochemical cell which has the high potential more than now, and spreading it widely has indispensable development of the new high surface area semiconductor electrode excellent in manufacturability, such as controllability and reproducibility.

[0006]By the way, wet process represented by the sol-gel method as a manufacturing method of semiconductor membrane, the semi-dry process represented by the SPD (Spray Pyrolysis Deposition) method and CVD (Chemical Vapor Deposition) -- the dry method etc. which are represented by law, sputtering process, and vacuum deposition are known.

[0007]Generally, although production of the precise high film of surface smoothness has been applicable in the semi-dry process and the dry method. Recently, the reports of production of a high surface area film were made by Okutani (a functional material, Vol.20, p.14-2000), Saito and others (high-performance material, Vol.19, p.5; (1999) JP,H10-152396,A).

[0008]Okutani and others uses the high surface area titanium oxide membrane which the needlelike micro crystallite of the titanium oxide produced by the SPD method deposited. The dye sensitizing type photoelectrochemical cell of about a little less than 2% of efficiency for light utilization. It has reported (The Extended.). Abstracts of "The 3 rd NIMO International Symposium on Photoreaction Control and Photofunctional Materials", p.222-2000. sol -- although the cause of the lowness of the efficiency in comparison with a thing with -\*\*\*\* system titanium oxide is not clarified, the titanium oxide membrane by the SPD method is a film which needlelike micro crystallite deposited at random.

Causes, like a pole diameter is small and electrolytic diffusibility is [ which it is not / specific surface area / enough ] low are guessed.

The SPD method sprays a raw material solution on a heating board from a nozzle, solvent evaporation and raw material decomposition oxidation are

made to perform on a substrate, it says that an organic solvent steam occurs so much, and also [ safe ] there is an environmental problem. A substrate cools by absorption of the evaporation heat accompanying solvent evaporation, and a measure, such as improving the capability of a heating heater to spray by an intermission, for earning thickness, is required, and it is accompanied by the fall of productivity, a cost hike, etc.

[0009]On the other hand, the method of Saito and others is a new method (it outlines the following "A-CVD method") of performing a CVD method by an atmosphere release system.

Compared with the conventional CVD method, it has an advantage, like a vacuum system is unnecessary and simplicity, ease [ continuation membrane formation ], and membrane formation speed of equipment are early. In order to steam-ize a raw material and to spray a substrate, the problem in the above-mentioned SPD method does not occur. It is shown clearly that a structure with the anisotropy which carried out crystal growth specifically can be easily formed in perpendicularly [ substrate ] it was called the whisker structure of mum order and mesh structure from nm by Saito's and others latest research.

[0010]

[Problem to be solved by the invention]However, the electrode which made the semiconductor structure thing produced by A-CVD method support a functional compound, It was a system which the example of an indication about the application what is called to a chemical modification semiconductor electrode does not have, and is remarkably different from what is called a conventional micro crystallite sintering type (all of a particle sintering process, a sol-gel method, and the SPD method go into this category fundamentally.) of thing, and was strange about that applicability. The titanium oxide membrane which has whisker structure by Saito and others is compared with the conventional titanium oxide membrane,

Remarkably, photocatalyst activity was high and it succeeded in the report etc. which are referred to as that the photolysis of the functional compounds, such as a pigment, is carried out easily (Jpn. Appl.Phys., vol.39, p.L169-2000), and it was considered if not suitable for use as a chemical modification semiconductor electrode.

[0011]This invention solves many problems in said conventional technology, and makes it SUBJECT to attain the following purposes. That is, the purpose of this invention is to provide the chemical modification semiconductor electrode excellent in the photoelectrical characteristic, endurance, safety, manufacturability, etc., its manufacturing method, and the photoelectric cell using it.

[0012]

[Means for solving problem]An aforementioned problem is solved by the following means. Namely, the pillar-shaped semiconductor group by which this invention was anisotropically arranged to <1> thickness direction. The fine pores continuously prolonged in the longitudinal direction of said pillar-shaped semiconductor formed of each gap between pillar-shaped semiconductors. It is a chemical modification semiconductor electrode, wherein it has the \*\*\*\* air quality semiconductor electrode layer or both the multi-air quality semiconductor electrode layer \*\* constituted and some or all of this pillar-shaped semiconductor group surface comes to support a functional compound.

[0013]<2> Each pillar-shaped semiconductor is a chemical modification semiconductor electrode given in the above <1> being ten or more anisotropy factors.

[0014]<3> Each pillar-shaped semiconductor is a chemical modification semiconductor electrode given in the above <1> or <2> which crosses or connects mutually, forms network structure, and is characterized by things.

[0015]<4> pillar-shaped semiconductor group contains at least one sort of

the metallic oxide chosen from titanium oxide, a zinc oxide, tin oxide, niobium oxide, and indium oxide, and is a chemical modification semiconductor electrode given in either of aforementioned <1>-<3> characterized by things.

[0016]On a piece [ of <5> ] multi-air quality semiconductor electrode layer, or both multi-air quality semiconductor electrode layer, both multi-air quality insulation layer is laminated, and it is a chemical modification semiconductor electrode given in either of aforementioned <1>-<4> characterized by things.

[0017]It is a manufacturing method of a chemical modification semiconductor electrode which manufactures a chemical modification semiconductor electrode of a description to either of <6> aforementioned <1>-<5>. It is a manufacturing method of a chemical modification semiconductor electrode having the process of spraying raw material metallic compounds evaporated or clustered and inactive gas on a heated substrate face under a steam atmosphere, and forming a pillar-shaped semiconductor group.

[0018]A process to which some or all of a pillar-shaped semiconductor surface is made to carry out chemical absorption of the silicon compound which is a manufacturing method of a chemical modification semiconductor electrode which manufactures a chemical modification semiconductor electrode of a description, and is expressed with a following general formula (1) to either of <7> aforementioned <1>-<5>. It is a manufacturing method of a chemical modification semiconductor electrode having a process which makes it join together chemically and makes some or all of the pillar-shaped semiconductor group surface support a pigment which has a termination group of said silicon compound, and a basis which can carry out a chemical bond.

[0019]A general formula (1)  $A_nR_{(3-n)}Si-L-X$  [0020](A expresses an aryloxy group which is not replaced [ an alkoxy group which is not replaced / a

halogen atom, substitution, or /, substitution, or ] among a general formula (1).) R expresses an aryl group which is not replaced [ an alkyl group which is not replaced / substitution or /, substitution, or ]. L expresses a divalent hydrocarbon group of the carbon numbers 1-20, and a divalent hetero atom content hydrocarbon group of the carbon numbers 1-20. X expresses a vinyl group which is not replaced [ a halogen atom, hydroxyl, an amino group, a carboxyl group, an epoxy group, an isocyanate group, a sulphydryl group, substitution, or ]. n expresses an integer of 1-3.

[0021]<8> It is a photoelectric cell which possesses at least a support electrode which laminates a conductive substrate and a chemical modification semiconductor electrode given in either of aforementioned <1>-<5>.

[0022]

[Mode for carrying out the invention] Hereafter, this invention is explained in detail. The person skilled in the art can add arbitrary change to an embodiment of the invention based on the conventional knowledge about a CVD method, photoelectricity chemistry, a cell, etc. A chemical modification semiconductor electrode of this invention is usually formed on a substrate according to a use.

[0023](Chemical modification semiconductor electrode) A chemical modification semiconductor electrode of this invention. A pillar-shaped semiconductor group anisotropically arranged to a thickness direction, and fine pores continuously prolonged in a longitudinal direction of said pillar-shaped semiconductor formed in a gap between these pillar-shaped semiconductors, It has a \*\*\*\* air quality semiconductor electrode layer or both multi-air quality semiconductor electrode layer (it may only be hereafter called a "semiconductor electrode layer") \*\* constituted, and some or all of this pillar-shaped semiconductor group surface comes to support a functional compound. A \*\*\*\* air quality semiconductor electrode

layer or both multi-air quality semiconductor electrode layer with which it comes to support a functional compound may be hereafter called "chemical modification semiconductor electrode layer."

[0024]Here, both many air quality is continuously prolonged in a longitudinal direction of a pillar-shaped semiconductor, and expresses structure where fine pores anisotropically penetrated from a membrane surface toward a rear face to a thickness direction exist by high density. \*\*\*\* air quality is continuously prolonged in a longitudinal direction of a pillar-shaped semiconductor, and expresses structure where fine pores of the shape of a dead end by which the closedown of one side was anisotropically carried out to a thickness direction with a semiconductor toward a rear face from a membrane surface exist by high density.

[0025]The chemical modification semiconductor electrode of this invention is that have the \*\*\*\* air quality or both the multi-air quality structure which comprised an above-mentioned specific pillar-shaped semiconductor group and fine pores formed by that cause, and some or all of this pillar-shaped semiconductor group surface comes to support a functional compound, and is excellent in the photoelectrical characteristic, endurance, safety, manufacturability, etc. Functional grant and highly-efficient-izing of spectral sensitization, blocking nature, stability, etc. are realizable by choosing a functional compound suitably. It is each pillar-shaped semiconductor in a pillar-shaped semiconductor group being anisotropically arranged to a thickness direction, and taking \*\*\*\* air quality or both multi-air quality structure, The charge transfer way which continued from the membrane surface to a rear face is secured, and the continuous mass transfer way is secured because the fine pores formed with this pillar-shaped semiconductor extend continuously in the longitudinal direction of this pillar-shaped semiconductor on the other hand. For this reason, since the charge transfer way which continued anisotropically is secured, charge

transfer is possible for the chemical modification semiconductor electrode of this invention barrier-free from a membrane surface to a rear face. On the other hand, since the mass transfer way which continued anisotropically is secured, a functional compound can be made to support uniformly even inside a semiconductor electrode layer. Functional compounds, such as paints with comparatively large particle diameter, can also be made to support, substances, such as an electrolyte, permeate even the inside of a semiconductor electrode layer easily, and diffusion can prevent the decomposition reaction by stagnation etc., etc. well.

[0026]Here, an example of a section of a thickness direction of a semiconductor electrode layer in a chemical modification semiconductor electrode of this invention is shown to drawing 1. An example of a section of a thickness direction of a semiconductor electrode layer obtained with a sol-gel method is shown in drawing 2. As for the semiconductor electrode layer 10 shown in drawing 2, a layer is formed by imperfect sintering of the particles 12. For this reason, a lot of dead end-like the fine pores 14 and the independent fine pores (fine pores wide opened by neither the surface nor rear face) 15 which the penetration fine pores 13 which go to a rear face from a layer surface move in a zigzag direction, and have not been penetrated toward a rear face from a layer surface exist. An electrolyte does not permeate, but vena contracta exists in the penetration fine pores 13 and the dead end-like fine pores 14, and the independent fine pores 15 are unsuitable as a mass transfer way. Contact between particles is also imperfect sintering and vena contracta will exist also about an electronic transition. On the other hand, the semiconductor electrode layer 1 shown in drawing 1 each pillar-shaped semiconductors 2, 3, and 4, it is growing up anisotropically to a thickness direction, as a result the penetration fine pores 5 also take an anisotropic form toward a rear face from a layer surface, and both charge transfer in each pillar-shaped semiconductors 2, 3, and 4

and mass transfer in the penetration fine pores 5 boil them markedly compared with a semiconductor electrode layer shown in drawing 2, and they become advantageous. Each pillar-shaped semiconductor 2 is a pillar-shaped semiconductor of a single crystal, each pillar-shaped semiconductor 4 is a pillar-shaped semiconductor of polycrystal, and a columnar body of two or more single crystals connects each pillar-shaped semiconductor 4.

[0027]As for each pillar-shaped semiconductor, in a semiconductor electrode layer, it is preferred that an anisotropy factor is ten or more. If this anisotropy factor is too small, significant nature to flat surfaces, such as high surface area, is not demonstrated, but problems, such as a functional grant fall etc. of a functional compound supported, may produce it. On the other hand, if too large, intensity falls and a problem of electrolytic mobility falling in application of a photoelectrochemical cell may arise. For this reason, if an anisotropy factor is ten or more, although it is satisfactory, by kind of functional compound, an application use, etc. When there is a more suitable range, and making a pillar-shaped semiconductor surface support a pigment as a functional compound and specifically applying a chemically modified electrode of this invention to a dye sensitizing type photoelectric cell, for example, as an anisotropy factor, 100 or more are preferred and they are 500-2000 more preferably.

[0028]Here, an anisotropy factor means average value of a value (X/Y) which \*\*(ed) length (X) of a thickness direction axis (major axis) in each pillar-shaped semiconductor by the length (Y) of a minor axis of a perpendicular direction section to a thickness direction.

[0029]In a semiconductor electrode layer, it is preferred that the average minimum diameter is 1 nm or more, it is not less than 5 nm more preferably, and fine pores formed with each pillar-shaped semiconductor are 10-100 nm still more preferably. If an average minimum diameter is too small, it becomes

difficult to make each pillar-shaped semiconductor surface in an inside of a semiconductor electrode layer support a functional compound uniformly, and in applying to a photoelectrochemical cell, a problem of an electrolyte not having permeated may arise. A minimum diameter here means the minimum of the length of a minor axis of a perpendicular direction section to a thickness direction. As long as it has extended continuously in a longitudinal direction of a pillar-shaped semiconductor, fine pores may be isolated or may be connected in part mutually.

[0030]In a semiconductor electrode layer, number density of a pillar-shaped semiconductor group to the project area. Although the higher one is preferred from a viewpoint of high-specific-surface-area-izing, it is determined by choosing suitably a size (form) of each pillar-shaped semiconductor, and a size (form) of fine pores formed of these from a pole diameter becoming small too much. If too high more than needed.

[0031]In a semiconductor electrode layer, each pillar-shaped semiconductor in a pillar-shaped semiconductor group, may form the shape of a pillar of a single crystal independently, and (for example, pillar-shaped semiconductor 2 grade in the pillar-shaped semiconductor electrode layer 1 shown in drawing 1), A crystal flake of arbitrary form (for example, rubbing [ the shape of \*\*, a flake, tabular etc. ]) is laminated, The shape of a pillar of polycrystal could be formed (for example, pillar-shaped semiconductor 3 grade in the pillar-shaped semiconductor electrode layer 1 shown in drawing 1), and an independent pillar-shaped single crystal may connect it (for example, pillar-shaped semiconductor 4 grade in the pillar-shaped semiconductor electrode layer 1 shown in drawing 1). [ two or more ]

[0032]In a semiconductor electrode layer, each pillar-shaped semiconductor in a pillar-shaped semiconductor group, Although which crystalline forms or these mixed state of amorphous one, polycrystal, and a single crystal can be taken, it may be precise or it may be porosity, it is preferred that it is in

precise polycrystal or a single crystal state in respect of conductivity, transparency, a mechanical strength, etc.

[0033]In a semiconductor electrode layer, although whisker shape structure may be formed independently mutually, and each pillar-shaped semiconductor may cross or connect mutually and may form meshes-of-a-net (mesh)-like structure, forming meshes-of-a-net (mesh)-like structure from a strong viewpoint has [ a pillar-shaped semiconductor group ] preferred things.

[0034]As for a pillar-shaped semiconductor group, in a semiconductor electrode layer, it is preferred to come to be formed with metal chalcogenide, such as a metallic oxide, metallic sulfide, and a metal selenide, and perovskites. as metal chalcogenide -- metal (for example, titanium, tin, zinc, and tungsten.) The oxide of metal, such as a zirconium, hafnium, strontium, indium, cerium, yttrium, a lanthanum, a ruthenium, vanadium, niobium, KADONIUMU, or tantalum, a sulfide, and a selenide are mentioned suitably. As perovskites. strontium titanate, titanic acid calcium, barium titanate, etc. are mentioned suitably. Containing also in these at least one sort of the metallic oxide chosen from titanium oxide, a zinc oxide, tin oxide, niobium oxide, and indium oxide has preferred things especially in respect of transparency, the photoelectrical characteristic. etc.

[0035]As for a semiconductor electrode layer, what has large surface area is preferred so that many functional compounds can be supported. For this reason, as for surface area of a semiconductor electrode layer, it is preferred that they are 10 or more times to a project area, it is more preferred that they are 100 or more times, and it is still more preferred that they are 500 or more times. Although there is no restriction in particular about a maximum of this surface area, since it leads to raising surface area as mentioned above making fine pores small, in a use which diffuses an electrolyte etc. and uses inside of fine pores, it usually becomes a maximum

as 5000 times.

[0036]As semiconductor electrode layer thickness, it is preferred that it is generally about 0.1-500 micrometers. When using as a photoelectric cell, it is preferred that it is 1-100 micrometers, and it is more preferred that it is 5-50 micrometers. Since specific surface area increases so that thickness of a semiconductor electrode layer increases, a capturing rate of light becomes high, but when using a pigment as a functional compound, since migration length of an electric charge poured in from the pigment increases, a loss by recombination also becomes large. Therefore, it is preferred to consider it as a mentioned range.

[0037]As a functional compound, it is suitably chosen by functions to give, such as a field to apply or spectral sensitization, blocking nature, and stability. For example, when applying to a spectral sensitization type (dye sensitizing type) photoelectric cell, as a functional compound, a pigment etc. which can give a function of spectral sensitization are mentioned, for example. When applying as cold cathode or an electron injection electrode, a silicon compound (structure where X in a general formula (1) mentioned later is fluoride) etc. which are shown in a following general formula (1) which has a fluorinated alkyl group which can give outstanding stability and an outstanding electrode characteristic by electronic suction nature as a functional compound are mentioned.

[0038]When using a pigment as a functional compound, it becomes possible [spectral sensitization] for a chemical modification semiconductor electrode of this invention, and light of long wavelength which does not have absorption in a semiconductor electrode layer can be used by this spectral sensitization. Since a semiconductor electrode layer takes multi-air quality structure and has high specific surface area, even if a pigment is monolayer absorption, a high light absorption amount will be realized.

[0039]As a pigment, the absorption wavelength is extended more than the

absorption end of a semiconductor electrode layer, and it is preferred that it is that from which sensitization is obtained in a wavelength band which a semiconductor electrode layer does not absorb. Specifically, indigo system compound [, such as metal chelate complex; porphyrin, its derivative; phthalocyanine and its derivatives, such as Ru, Os, Pt, nickel, Eu, Nd, Fe, Mn, Zn, Ti, Mg, Pd, Cu, and V, Quinacridone, and pyrrolo pyrrole, ]; etc. are mentioned, for example. As an example of a metal chelate complex, Ru bipyridyl system complex of a description is suitably mentioned to a U.S. Pat. No. 4927721 item Description, "a next-generation dye sensitizing type solar cell, its technology trends" (the Heisei 10(1998) new-materials Engineering Department meeting investigation report, Association for the Progress of New Chemistry), etc.

[0040]It is preferred that it is that where a pigment has a termination group of a silicon compound shown in the molecule by a basis or a general formula (1) which can carry out an ester bond to metallic-oxide structure of a pillar-shaped semiconductor surface, and a basis which can carry out a chemical bond, and chemical absorption is made in a semiconductor surface (a support method of a pigment is mentioned later). As a desirable example of such a basis, a vinyl group etc. which is not replaced [ a halogen atom, hydroxyl, an amino group, a carboxyl group, an epoxy group, an isocyanate group, a sulphydryl group, a pyridyl group a sulfonic acid group, a phosphate group and substitution, or ] are mentioned. Although a covalent bond, a coordinate bond, a hydrogen bond, and an ionic bond are mentioned as a chemical bond, it is a point of bond strength and a covalent bond and a coordinate bond are preferred.

[0041]A pigment may be used by an one-sort independent and may be used together two or more sorts. When a use is a dye sensitizing type photoelectric cell, it is preferred to cover the luminescence region of the light source to be used and to make the wavelength band of photoelectric

conversion large as much as possible, and expansion of a wavelength band can be easily aimed at by using together two or more sorts of pigments. However, there is affinity in the combination of a pigment, and when what has the sensitization effect separately when combination is mistaken is combined, the sensitization effect may decrease remarkably. This cause is not clarified but there is no other way but actual to depend. Also in the combination which the sensitization effect reduces remarkably only by carrying out coadsorption simply. Lamination adsorption may be able to be carried out in a suitable order, problems, such as reduction of the sensitization effect and photocatalytic degradation, may be able to be controlled by the policy of \*\* to which coadsorption (support) of the 3rd suitable adsorbent is carried out, or improvement in the photoelectrical characteristic etc. may be able to be aimed at. Specifically, a harmful interaction which the sensitization effect reduces by meeting of pigments can be inhibited by carrying out coadsorption of other compounds with a pigment (as a compound effective in this purpose). After making a stable functional compound cover to; photolysis to which the steroid compound (for example, cholic acid) etc. which have a carboxyl group are mentioned (support), even if it irradiates with the light of the wavelength which a semiconductor absorbs by supporting a pigment, the photocatalytic degradation of a pigment can be reduced. ; The compounds (for example, long chain fatty acid, long chain phosphoric ester, etc.) which have self-organization ability with a pigment by carrying out coadsorption. The stacking tendency of a pigment is controllable, and after making: pigment whose photoelectrical characteristic may improve adsorb, a non-adsorption site can be closed by using processing agents, such as an alkoxy silane compound, a chlorosilicane compound, amines, and thiols, and processing a semiconductor electrode. as the example of these processing agent -- hexyl trimethoxysilane and cyclohexyldimethyl methoxysilane.

Benzyltrichlorosilane, 4-tert-butylphenyl dimethylchlorosilane, pyridine, 4-tert-butylpyridine, polyvinyl pyridine, alpha mercaptodecane, etc. are mentioned. When these are liquids, it may use as it is. and it may dissolve and use for an organic solvent.: etc. are mentioned.

[0042]In the manufacturing method of the chemical modification semiconductor electrode of this invention, the support method of a functional compound is explained in detail.

[0043]Laminating both the multi-air quality insulation layer on a semiconductor electrode layer has [ the chemical modification semiconductor electrode of this invention ] preferred things. Both the multi-air quality insulation layer is provided in the puncturing side in a semiconductor electrode layer in the same structure as the above-mentioned chemical modification semiconductor electrode layer. As for both the multi-air quality insulation layer, forming continuously by the same operation is [ after forming a semiconductor electrode layer ] preferred. By this, the fine pores in a semiconductor electrode layer and the fine pores in both the multi-air quality insulation layer will be connected continuously, mass transfer ways, such as an electrolysis solution, will be secured, and it is desirable. As both this multi-air quality insulation layer material, a silicon oxide, an aluminum oxide, zirconium oxide, magnesium oxide, etc. are mentioned. Both this multi-air quality insulation layer plays a role of the high stability at the time of applying the photoelectric cell of this invention mentioned later to a photoelectrochemical cell, and the inorganic separator of high intensity. It is preferred to be carried out like the semiconductor electrode stratification process in the manufacturing method of the chemical modification semiconductor electrode of this invention mentioned later as a formation method of both the multi-air quality insulation layer.

[0044]Although the chemical modification semiconductor electrode of this

invention is applicable to electroluminescence devices, tunnel diode, cold cathode, a photoelectrochemical cell, a Schottky barrier type photoelectric cell, a p/n assembling-die photoelectric cell, etc., it is suitably applicable to a dye sensitizing type photoelectric cell especially.

[0045](Manufacturing method of a chemical modification semiconductor electrode) This invention is characterized by the manufacturing method of a chemical modification semiconductor electrode comprising the following. It is how to manufacture the chemical modification semiconductor electrode of said this invention, and is a semiconductor electrode stratification process.

Functional compound support process.

It may have other processes if needed.

[0046]As long as a semiconductor electrode stratification process gives structure with a preferred semiconductor electrode layer in the chemical modification semiconductor electrode of said this invention, what kind of process (method) may be sufficient as it, but. As a method of making it possible theoretically, A-CVD method and the anode oxidation method which are characterized by anisotropy reactions, such as different direction growth and the different direction dissolution, the Electrochemistry Sub-Division induction chemical deposition method, etc. are mentioned. Especially A-CVD method that is a kind of a CVD method also in these is preferred. Since a CVD method is performed by an atmosphere release system, and material gas (raw material metallic compounds) can be supplied at high concentration and deposition growth is performed with a molecular level, A-CVD method can form easily the pillar-shaped semiconductor anisotropically grown-up to the sedimentation trend (thickness direction (a substrate and a perpendicular direction)). About the A-CVD method itself, it is reported in detail by Saito and others in above-mentioned document, and all of those knowledge can be diverted. It is one of the manufacturing methods which the

\*\*\*\* air quality or both the multi-air quality structure itself in the semiconductor electrode layer in above-mentioned this invention governs device properties, such as the photoelectrical characteristic, and especially A-CVD method can embody it at, and was excellent in manufacturability, such as mass production nature and equipment simple nature. However, although what a substrate can be set for under the atmosphere is an advantage of A-CVD method, there is not necessarily the necessity of being under the atmosphere and enough steams required for hydrolysis of raw material metallic compounds should just exist.

[0047]It is preferred to perform a process of spraying concretely raw material metallic compounds and inactive gas which were evaporated or clustered on a substrate face under a steam atmosphere as a semiconductor electrode stratification process, and forming a pillar-shaped semiconductor group.

[0048]. In a semiconductor electrode stratification process, are heating raw material metallic compounds, make it evaporate or cluster, convey with inactive gas, such as dry nitrogen, and make it blow off from a nozzle. At this time, conveyance concentration of raw material metallic compounds is controllable by controlling cooking temperature, an inert gas flow rate, etc.

[0049]In a semiconductor electrode stratification process, raw material metallic compounds which blew off from a nozzle are hydrolyzed by steam in a steam atmosphere, and a pillar-shaped semiconductor group is formed by polymerizing in a substrate face. As for a substrate, at this time, being heated is preferred. Although this substrate temperature changes with a kind of raw material metallic compounds, or fine structures of a semiconductor electrode layer which consists of a pillar-shaped semiconductor group considered as a request and cannot generally be said, it is preferred that it is generally within the limits of 100 to 800 \*\*.

[0050]Although a semiconductor electrode stratification process is

performed under a steam atmosphere. As the steam partial pressure, 13.33 Pa ~ 6665 Pa (0.1mmHg ~ 50mmHg) are preferred, and is 266.3 Pa ~ 933.1 Pa (2mmHg ~ 7mmHg) still more preferably 133.3 Pa ~ 1333 Pa (1mmHg ~ 10mmHg) more preferably. A problem of the crystallinity of a semiconductor electrode layer which consists of a pillar-shaped semiconductor group obtained by hydrolyzing of raw material metallic compounds becoming that this steam partial pressure is less than 13.33 Pa insufficient falling may arise. On the other hand, if it exceeds 6665 Pa, problems, such as blinding of a nozzle which supplies raw material metallic compounds, may arise.

[0051]It is supplying raw material metallic compounds on a substrate directly in a semiconductor electrode stratification process. Both multi-air quality semiconductor electrode layer that consists of a pillar-shaped semiconductor group can be formed, and a \*\*\*\* air quality semiconductor electrode layer which consists of a pillar-shaped semiconductor group can be formed by supplying raw material metallic compounds on a substrate which provided a precise semiconductor layer beforehand. The same kind and any of a different kind may be sufficient as a semiconductor kind of this semiconductor layer and a pillar-shaped semiconductor group.

[0052]In a semiconductor electrode stratification process, it is supplying only raw material metallic compounds and inactive gas, and it is possible to form a semiconductor electrode layer which consists of a pillar-shaped semiconductor group. It is also possible to form a semiconductor electrode layer which consists of pillar-shaped semiconductor groups, such as metal nitride and metallic sulfide, by choosing raw material metallic compounds suitably, and using together gas, such as nitrogen, ammonia, and hydrogen sulfide, with this.

[0053]In a semiconductor electrode stratification process, metal chelate compound which has at least one or more chelate ligand, such as metal alkoxide; metal carboxylate;beta-diketones, beta-keto acid, and catechols,

is mentioned as raw material metallic compounds. Also in these, metal chelate compound is especially preferred in respect of storage stability, volatility, etc. These raw material metallic compounds may be used by an one-sort independent, and may be used together two or more sorts.

[0054]In a semiconductor electrode stratification process, it is the purpose of improvement in intensity, conductive improvement, and adsorbent Hitoshi Kougami of the functional compound mentioned later after the semiconductor electrode stratification, and various processings, such as annealing processing, washing processing, a chemical treatment, grinding treatment, and partial sealing, can be performed.

[0055]Although a functional compound support process is a process which makes some or all of a pillar-shaped semiconductor surface support a functional compound. Although the method of carrying out chemical absorption of the functional compound in a monomolecular layer, the method of carrying out multilayer adsorption of the functional compound, the method of embedding a functional compound in fine pores, etc. are specifically mentioned, it is points, such as endurance and charge separation efficiency, and it is preferred to carry out chemical absorption in a monomolecular layer. When using a pigment as a functional compound especially, the pigment which has a basis which can carry out an ester bond to the metallic-oxide structure of a pillar-shaped semiconductor surface is used. It is desirable at the point which says that adsorption intensity with high method of carrying out chemical absorption (chemistry immobilization) and method of carrying out chemistry immobilization via it using a silicon compound and adsorption density are easily realizable, and the method of carrying out chemical absorption (chemistry immobilization) especially using a silicon compound is preferred.

[0056]The silicon compound support process of making some or all of the pillar-shaped semiconductor group surface supporting the silicon compound

expressed with a following general formula (1) when specifically using a pigment as a functional compound as a functional compound support process. Especially the thing for which the pigment support process of making it joining together chemically and making some or all of the pillar-shaped semiconductor group surface supporting the pigment which has a termination group of this silicon compound and a basis which can carry out a chemical bond is performed is preferred.

[0057]A general formula (1)  $A_nR_{(3-n)}Si-L-X$  [0058](A expresses an aryloxy group which is not replaced [ an alkoxy group which is not replaced / a halogen atom, substitution, or /, substitution, or ] among a general formula (1).) R expresses an aryl group which is not replaced [ an alkyl group which is not replaced / substitution or /, substitution, or ] (an alkyl group which is not replaced [ substitution of the carbon numbers 1-6 or ] is expressed preferably.). L expresses a divalent hydrocarbon group of the carbon numbers 1-20, and a divalent hetero atom content hydrocarbon group of the carbon numbers 1-20. X expresses a vinyl group which is not replaced [ a halogen atom, hydroxyl, an amino group, a carboxyl group, an epoxy group, an isocyanate group, a sulphydryl group, substitution, or ]. n expresses an integer of 1-3.

[0059]in a functional compound support process, a silicon compound expressed with a general formula (1), Generally by which basis a connecting group combines with a pillar-shaped semiconductor surface by having two sorts (X basis and  $A_nSi$  group) joins together with an  $A_nSi$  group in many cases, although it differs from combination of X basis and an  $A_nSi$  group according to a pillar-shaped semiconductor kind and its surface structure and cannot generally say. Depending on combination of X basis and an  $A_nSi$  group, and a processing condition at the time of adsorption, both bases are chemisorbed in a pillar-shaped semiconductor surface, and since there is a case where it becomes impossible to already connect a pigment, cautions

are required. When using a metallic oxide as a pillar-shaped semiconductor, especially a desirable combination of X basis and an A<sub>n</sub>Si group. It is the combination of Br basis or I basis, and Cl<sub>n</sub>Si or (R'O)<sub>n</sub>Si (R' shows here an aryl group which is not replaced [ an alkyl group which is not replaced / substitution or /, substitution, or ].). There is almost no adsorptivity of Br basis on the surface of a metallic oxide and I basis to reactivity on the surface of a metallic oxide carrying out firm chemical absorption easily highly, as for Cl<sub>n</sub>Si and (R'O)<sub>n</sub>Si. Therefore, free Br basis and I basis can remain and chemistry immobilization of the pigment can be easily carried out by using a pigment which has this Br basis, I basis, and a basis that can carry out reaction substitution.

[0060]In a functional compound support process, the above-mentioned silicon compound support process and a pigment support process, Dissolve or distribute a silicon compound or a pigment expressed with a general formula (1) in a respectively suitable solvent, and a stain solution is prepared. How to spray a semiconductor electrode layer in a method; stain solution which immerses a semiconductor electrode layer into this stain solution; method; etc. which apply a stain solution by spin coat method, the blade coat method, etc. on a semiconductor electrode layer can perform. It is high, and there is also little futility of a stain solution, and a dip dyeing method which immerses a semiconductor electrode layer into a stain solution also in these has especially preferred mass production nature. It also has an advantage which says that a dip dyeing method is heating a stain solution or generating an ultrasonic wave, and can accelerate an adsorption reaction. As for an unadsorbed pigment, removing by post-washing is preferred.

[0061](Photoelectric cell) A photoelectric cell of this invention possesses a support electrode which laminates a conductive substrate and a chemical modification semiconductor electrode of said this invention at least. Although a photoelectric cell of this invention is applicable as various

photoelectric cells, it becomes being the composition of, for example, providing an electrolyte pinched between this support electrode, a counterelectrode, and this support electrode and a counterelectrode with application to a photoelectricity chemistry photoelectric cell. It becomes being the composition which consists of this support electrode and a counterelectrode with application to a shot key type photoelectric cell. When a pigment is used as a functional compound made to support in a chemical modification semiconductor electrode of said this invention, it becomes a dye sensitizing type photoelectric cell.

[0062]In the photoelectric cell of this invention, in order for light to reach the chemical modification semiconductor electrode in a support electrode, either [ at least ] the conductive substrate in the above-mentioned support electrode or a counterelectrode must be substantially transparent. In the photoelectric cell of this invention, the conductive substrate in a support electrode is transparent or translucent, and it is preferred that it is the composition of entering use lights, such as sunlight, from the support electrode side. That it is transparency (transparent or translucent) substantially means that the transmissivity of light to use is not less than 10%, it is preferred that it is not less than 50%, and it is preferred that it is especially not less than 75%.

[0063]A support electrode laminates a conductive substrate and the chemical modification semiconductor electrode of said this invention, and although, What was formed as this conductive substrate with metal (for example, iron, platinum, gold, silver, copper, aluminum, rhodium, indium, nickel, titanium, a zirconium, etc.); thing [ in which the conductive layer was formed on the surface of the base substance ]: etc. are mentioned. In the case of the latter, as a base substance, arbitrary things, such as Ceramics Sub-Division, glass, and a plastic, are mentioned. moreover -- as conductive layer material -- metal (for example, platinum, gold, silver, copper, and

aluminum.) Carbon, such as rhodium, indium, nickel, titanium, and a zirconium, Conductive metallic oxide (what doped fluoride to an indium tin multiple oxide, an indium zinc multiple oxide, and diacid-ized tin, the thing which doped aluminum to the zinc oxide, the thing which doped niobium to titanium oxide, etc.) is mentioned. Also in these, the thing in which conductive metallic oxide with the high permeability of visible light was formed on glass or the base substance made of resin is preferred. If the thickness of this conductive layer can secure sufficient conductivity, there will be no restriction in particular of thickness, but it is preferred that they are generally 10 nm - about 5 micrometers. When forming a conductive layer on a base substance, anythings are available for the formation method, for example, vacuum deposition, sputtering process, a CVD method, a sol-gel method, the SPD method, etc. are mentioned. Although what kind of thing may be sufficient about the structure of a conductive layer, light is not scattered about, and it is desirable for a mechanical strength to be high, and it is preferred that it is a precise and flat structure.

[0064]Although resistance of a conductive substrate is so preferred that it is low, it is preferred that a value of surface resistance is specifically below 100 ohm/cm<sup>2</sup>, and below 50 ohm/cm<sup>2</sup> is below 10 ohm/cm<sup>2</sup> still more preferably more preferably.

[0065]Although a support electrode is producible by forming a chemical modification semiconductor electrode (layer) as mentioned above on a conductive substrate, For the purpose of making both adhesion improve etc., a special intermediate layer can be provided between a conductive substrate and a chemical modification semiconductor electrode, or arbitrary processings of electrolytic oxidation processing, a chemical treatment, mechanical grinding treatment, etc. can also be performed to the conductive substrate surface. What has the adhesion of the thing; conductive substrate and a chemical modification semiconductor electrode which ease lattice

mismatching of a conductive substrate and a chemical modification semiconductor electrode high as an intermediate layer; A chemical modification semiconductor electrode from a conductive substrate, Or what [ blocks mass transfer from a chemical modification semiconductor electrode to a conductive substrate which is not desired ]; etc. are mentioned.

[0066]A counterelectrode works as a counter electrode of a support electrode. A counterelectrode does not necessarily need to give intensity, although the same thing as the above-mentioned conductive substrate is usually used. In a photoelectric cell of this invention, it is preferred that a conductive substrate in a support electrode is the composition of it being transparent or translucent and entering use lights, such as sunlight, from the support electrode side, and it is more preferred that a counterelectrode has the character to reflect light, in that case.

[0067]As a counterelectrode, a thin layer of metal; metal or a conductive oxide Vacuum deposition, Glass, Ceramics Sub-Division, or a plastic formed with sputtering process, a CVD method, the SPD method, plating, a sol-gel method, screen printing, etc.; thing [ which made glass, plastics, etc. distribute conductive substances, such as carbon black and a conductive oxide, ]; etc. are mentioned. Also in these, glass or plastics which provided a platinum thin film in the outermost surface is preferred in respect of electrochemical stability, cost, etc.

[0068]it is preferred to use a stable redox couple in the field of Electrochemistry Sub-Division, as an electrolyte, at a point referred to as to be able to operate as a reproduced type photoelectrochemical cell, although publicly known arbitrary things are available.

[0069]As a redox couple, they are iodine and a metal iodide ( ). [ LiI, NaI, KI and ] An iodide salt of; iodine, such as CsI and CsI<sub>2</sub>, the iodine salt; iodine of the 4th class imidazolium compounds, the iodide salt; iodine of the 4th class

pyridinium compound, and a tetraalkylammonium compound; bromine and a metal bromide ( ) [ LiBr and ] NaBr, KBr, CsBr, ;, such as CaBr<sub>2</sub>, -- bromide salt [ of bromine and the 4th class imidazolium compounds ]; -- bromide salt [ of bromine and the 4th class pyridinium compound ]; -- bromide salt [ of bromine and a tetraalkylammonium compound ]; -- ferrocyanic acid salt and ferricyanic acid salt; -- ferrocene and a ferro SHINIUMU ion salt. An alkyl thiol and alkyl disulfide; hydroquinone and quinone; etc. are mentioned. Also in these, especially a redox couple of iodine and an iodine salt is preferred. [0070]An electrolyte is an advantage of being easy to permeate the fine pores in a chemical modification semiconductor electrode layer from which high conductivity is acquired, and it is preferred to use in the state (henceforth an "electrolysis solution") where it was made to dissolve or distribute in a suitable solvent. As a solvent, in the field of Electrochemistry Sub-Division, although a publicly known solvent is available, the nonaqueous system organic solvent used especially with a lithium ion battery can divert suitably. Generally, it is preferred that a dielectric constant is high in improving the mobility of a solute low, and viscosity is what improves dissociative [ of a salt ] and can reveal the outstanding ion conductivity. It is preferred that it is stable to a photoelectrochemical reaction. Specifically Cyclic carbonate; dimethyl carbonate, such as ethylene carbonate, propylene carbonate, and butylene carbonate. Non-cyclic carbonate, such as diethyl carbonate and methylethyl carbonate; Dioxane, A tetrahydrofuran, 2-methyltetrahydrofuran, ethylene glycol dialkyl ether, Propylene glycol dialkyl ether, polyethylene-glycol dialkyl ether, Ether, such as polypropylene-glycol dialkyl ether; Acetonitrile, Guru taro dinitrile, methoxy acetonitrile, propionitrile, Nitril, such as benzonitrile; Ester species; dimethylformamides, such as sulfoxide;gamma butyrolactones, such as dimethyl sulfoxide and sulfolane. Heterocyclic, such as amide:3-methyl-2-oxazolidinone, such as dimethylacetamide and N-methyl

pyrrolidone, is mentioned. Although the solvent of this may be used independently, it is preferred to use two or more sorts together. As such a combination, hyperviscosity and a lower dielectric constant solvent (for example, ethylene carbonate, propylene carbonate, dimethyl sulfoxide, sulfolane, etc.). Combination with hypoviscosity and high permittivity solvents (for example, acetonitrile, ethylene glycol dimethoxyether, 2-methyltetrahydrofuran, diethyl carbonate, etc.) is mentioned.

[0071]As concentration of an electrolyte in an electrolysis solution, it is preferred that they are 0.01mol/L - 2 mol/L, and it is more preferred that they are 0.1 mol/L - 1 mol/L. Although either an oxidant or a reduced form may be added as an electrolyte at the time of cell production, both an oxidant and a reduced form may be added simultaneously. in this case -- as opposed to a reduced form -- an oxidant -- 5-mol% - 20-mol% -- it is preferred to consider it as an added system. When there is too little electrolytic concentration, the conductivity of an electrolysis solution becomes insufficient, there are things, and when electrolytic concentration is too large conversely, conductive improvement may not come out so much and material not only becomes useless, but it may produce a problem of crystallization. .

[0072]A wettability improving agent for making a gelling agent for making an electrolysis solution pseudo-solidify a viscosity controlling agent for raising a salt for raising ionic conduction nature etc. further and the ease of treating of liquid and liquid and perviousness to semiconductor fine pores improve, etc. can also be added. Gel means the state where a colloidal particle or a solute lost motility which became independent for an interaction, and solidified with structure which gathered. In this invention, although a polymer gelling agent and low molecule gelling agent is also available, J.

Chem.Soc.Japan, Ind.Chem.Soc., Vol.46, p.779-1943;J.Am.Chem.Soc., Vol.111, p.5542-1989;J.Chem.Soc., Chem.Commun., p.390-1993.

Angew.Chem.Int.Ed.Engl., Dibenzylidene-D-sorbitol given in Vol.35, p.1949-1996;Chem.Lett., p.885-1996;J.Chem.Soc., Chem.Commun., and p.545-1997 grade, A cholesterol derivative, an amino acid derivative, an alkylamide derivative of a trans-(R [ 1 ], 2R)-1,2-cyclohexanediamine, Low molecule gelling agents, such as an alkylurea derivative, N-octyl-D-guru KONAMIDO benzoate, and a dual leadership type amino acid derivative, are suitably available. It is choosing suitably a kind of gelling agent to be used, a kind of solvent, and concentration, in order that a solution which added these low molecule gelling agents may have mobility at an elevated temperature and may gel it at low temperature. Gelation temperature is controlled, and the pouring-in characteristic as liquid in a heating flow state can be secured at the time of cell production, and a problem of disclosure of an electrolysis solution as a gelling solid is solved at the time of cell use. [0073]The electrolysis solution can provide a gap suitable between a support electrode and a counterelectrode, and can be made to pinch it between a support electrode and a counterelectrode by being poured in into it. As a method of forming a gap, How to \*\* to \*\* insulating inorganic powder, such as silica which a field of a liquid crystal display may be sufficient as, and is used; Insulating resin films, such as a Teflon (registered trademark) sheet which cut an opening of electrode shape, are made into a spacer. How to make it intervene; Polypropylene which has many penetration fine holes of a submicron order which may call a separator and is used in the field of a lithium ion battery. How to use an organic separator of insulating resin films, such as polyethylene; method; etc. between which both multi-air quality insulation layer formed on a chemical modification semiconductor layer in a chemical modification semiconductor electrode of this invention mentioned above is made to be placed as a separator can be used. In a method of using a spacer, when the external pressure is applied, two electrodes contact and short-circuit. Or a grade of an outflow of an electrolysis solution at the time

of damaging, since it does not occur and an electrolysis solution is supported with surface tension by fine void of a problem of an electrode contact short circuit according to the external pressure with a method of using a separator to a problem of an electrolysis solution flowing arising when a cell is damaged is also light. However, a problem of a volume change by swelling by an organic solvent in an electrolysis solution and a problem which said that it was difficult for a wettability to an electrolysis solution to make an electrolysis solution permeate separator fine pores bad may produce polypropylene and an organic separator made from polyethylene. Although it succeeds in examination which processes the surface of a separator and gives polarity in order to improve a wettability, In order for this to worsen a problem of swelling by an organic solvent and to reduce the electrochemical stability of a separator further, even if a problem does not actualize, for a single-use lithium ion battery use, there is a possibility of causing a fall of a life, by a reproduced type photoelectric cell use. For this reason, especially a thing made for both multi-air quality insulation layer of the same structure as this to intervene as an inorganic separator from knowledge of a chemical modification semiconductor electrode layer mentioned above is preferred.

[0074]Although restrictions in particular do not have it, when using an above-mentioned spacer and organic separator, the ranges of it are 1 micrometer - 1 mm, and when using an inorganic separator, the range of 0.1 micrometer - 0.1 mm is generally preferred [ the interval of a support electrode and a counterelectrode ]. A spacer, an organic separator, and an inorganic separator may be used independently, or may combine and use them.

[0075]The photoelectric cell of this invention is designed according to the purpose, generally connects two or more photoelectric cells, and is used. The size of each photoelectric cell is arbitrary, and two or more

photoelectric cells may be produced on the same base material, or may be produced on a respectively separate base material. It can also be considered as multilayered constitution. Even if the functional compound in the chemical modification semiconductor electrode of each photoelectric cell uses the same thing by all the photoelectric cells, it may use things different, respectively. It is preferred to cover the whole surface or a part of photoelectric cell in the photoelectric cell of this invention with the polymer which added various additive agents if needed, adhesives, etc. for the purposes, such as deterioration prevention by prevention of the crack to an entrance plane, oxidation of a structure, etc., electrolytic leakage control, and prevention from incidence of ultraviolet rays.

[0076]

[Working example]Hereafter, an embodiment is given and this invention is explained still more concretely. However, these each embodiment does not restrict this invention.

[0077][The example 1 of production]

- On production-fluoride dope tin oxide transparent conductive layer coat glass (made by Asahi Glass Co., Ltd.) (conductive substrate) of both multi-air quality titanium oxide semiconductor electrode layer, With reference to document of Saito and others mentioned above, both multi-air quality titanium oxide layer of 5 micrometers of thickness was produced with A-CVD system (product made from the Asahi engineering) under steam partial pressure the atmosphere of 933.1 Pa (7mmHg). Substrate temperature was 450 \*\*, using tetraisopropoxy titanium as a titanium material, and membrane formation time was 4 minutes. A minor axis of a perpendicular direction section an obtained titanium oxide layer (semiconductor electrode layer) to a thickness direction Tens of nm, A hundreds of nm pillar-shaped semiconductor group crosses or connects anisotropically and mutually to a thickness direction a major axis is formed

in mesh shape (mesh state), and a minimum diameter in a minor axis of a perpendicular direction section to a thickness direction by tens of nm. It had both the multi-air quality structure where fine pores prolonged continuously were innumerable formed in a longitudinal direction of each pillar-shaped semiconductor. An anisotropy factor of each pillar-shaped semiconductor was about 200.

[0078][The example 2 of production]

- Production of both multi-air quality titanium oxide semiconductor layer of the example 1 of production-production of both the multi-air quality titanium oxide semiconductor electrode layer / both multi-air quality zirconium oxide insulation layer is followed, 2 micrometers of both multi-air quality zirconium oxide insulation layers were made to laminate on both multi-air quality titanium oxide semiconductor electrode like the example 1 of production except having changed raw material metallic compounds into a tetra isopropoxy zirconium from tetraisopropoxy titanium.

[0079](Embodiment 1)

Conductive layer coat glass (conductive substrate) which provided both multi-air quality titanium oxide semiconductor electrode layer obtained in the example 1 of production-production of a <production of support electrode 1>-pigment support semiconductor electrode, It was immersed in an ethanol solution ( $3 \times 10^{-4}$  mol/L) of an  $\text{Ru}(4,4'\text{-dicarboxybipyridyl})_2(\text{NCS})_2$  pigment at 50 \*\* for 24 hours. Natural seasoning of this conductive layer coat glass was washed and carried out by ethanol, and a pigment was made to stick to both multi-air quality titanium oxide semiconductor electrode layer. Thus, the support electrode 1 which consists of conductive layer coat glass which provided a pigment support semiconductor electrode was produced. Absorption of a place which measured an electronic absorption spectrum of an obtained pigment support semiconductor electrode, and a visible portion characteristic of a pigment to be sure was shown.

[0080](Embodiment 2)

Instead of conductive layer coat glass which provided both multi-air quality titanium oxide semiconductor electrode layer obtained in the example 1 of production-production of a <production of support electrode 2>-pigment support semiconductor electrode, A pigment was made to adsorb like Embodiment 1 except having used conductive layer coat glass which provided both multi-air quality titanium oxide semiconductor layer and both multi-air quality zirconium oxide insulation layer which were obtained in the example 2 of production one by one. Thus, the support electrode 2 which consists of conductive layer coat glass which provided a pigment support semiconductor electrode was produced. Absorption of a place which measured an electronic absorption spectrum of an obtained pigment support semiconductor electrode, and a visible portion characteristic of a pigment to be sure was shown.

[0081](Embodiment 3)

The conductive layer coat glass which provided both the multi-air quality titanium oxide semiconductor electrode layer obtained in the example 1 of production-production of the pigment support semiconductor electrode using a <production of support electrode 3>-linking agent was immersed in the carbon tetrachloride solution ( $1 \times 10^{-3}$ mol/L) of gamma-bromopropyl trichlorosilane at the room temperature for 3 hours. Then, natural seasoning was washed and carried out with a carbon tetrachloride and acetone. Next, it was immersed in the dimethylacetamide solution ( $1 \times 10^{-5}$ mol/L) of the Ru(4,4'-dicarboxybipyridyl)<sub>2</sub>(NCS)<sub>2</sub> pigment, and dyeing processing was carried out at 95 \*\* under nitrogen air current protection from light for 36 hours. Natural seasoning of this conductive layer coat glass was washed and carried out by ethanol, and the pigment was made to stick to both the multi-air quality titanium oxide semiconductor electrode layer. Thus, the support electrode 3 which consists of conductive layer coat glass which

provided the pigment support semiconductor electrode was produced. Absorption of the place which measured the electronic absorption spectrum of the obtained pigment support semiconductor electrode, and the visible portion characteristic of a pigment to be sure was shown.

[0082](Embodiment 4)

The support electrode 1 (semiconductor electrode side) obtained in <production of dye sensitizing type photoelectric cell 1> embodiment 1. The glass surface was made to sandwich the counterelectrode in which platinum was made to form by sputtering process via the silicon-oxide spacer of the diameter of 10 micrometer, the electrolysis solution was poured into the gap by osmometry, and the photoregeneration type photoelectrochemical cell was produced. As an electrolysis solution, what dissolved tetrabutylammonium iodide and iodine in the propylene carbonate / ethylene carbonate partially aromatic solvent whose volume ratio is 1/1 so that each concentration might be set to 0.45mol/L, and 0.05 mol / L was used. When the obtained photoregeneration type photoelectrochemical cell was set in the usual evaluation system and it irradiated with the false sunlight of 100 W/m<sup>2</sup> in the solar simulator from the support electrode side, eta (efficiency for light utilization) is 4%, and it turned out that it is useful as a photoelectric cell.

[0083](Embodiment 5)

Except having used the support electrode 3 obtained in Embodiment 3 instead of the support electrode 1 obtained in <production of dye sensitizing type photoelectric cell 2> embodiment 1, a photoregeneration type photoelectrochemical cell was produced like Embodiment 4, and it evaluated like Embodiment 4. eta is 5% and it turned out that it is useful as a photoelectric cell.

[0084](Embodiment 6)

The same electrolysis solution as having used in Embodiment 4 on the

support electrode 3 obtained in <production of dye sensitizing type photoelectric cell 3> embodiment 2 (the semiconductor electrode side) was hung down, from on the, a counterelectrode which made platinum form in the polyimide film surface by sputtering process was piled up, and a photoregeneration type photoelectrochemical cell was produced. A place and eta which evaluated this photoregeneration type photoelectrochemical cell like Embodiment 4 were 4%. It turned out high durability [ a place and eta which evaluated this photoregeneration type photoelectricity chemistry of this in a similar manner after neglect for one month in a room temperature and the atmosphere and under dark ] are 4% and useful as a photoelectric cell.

[0085]From Embodiments 1-6, a chemical modification semiconductor electrode which made a pigment support as a functional compound, It has detailed \*\*\*\* air quality or both multi-air quality structure, a high light absorption amount and fine pores of sufficient size for substance diffusion are combined, and it turns out that an effect which says that a dye sensitizing type photoelectric cell using this demonstrates the outstanding photoelectrical characteristic and high endurance and which stood high is done so. By utilizing A-CVD method, at high speed, reproducibility is good and a suitable multi-air quality semiconductor electrode layer and a multi-air quality insulation layer for this invention can be produced. Since a still more suitable semi-conductive base material (transparent conductive layer) for this invention is also producible, manufacture of a photoelectric cell which carried out continuation consistency is possible, and it is dramatically promising in respect of mass production nature and low-cost-izing.

[0086]

[Effect of the Invention]According to this invention, by the above, the chemical modification semiconductor electrode excellent in the

photoelectrical characteristic, endurance, safety, manufacturability, etc., its manufacturing method, and the photoelectric cell using it can be provided.

[Translation done.]